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# PATENT SPECIFICATION



805,586

Date of Application and filing Complete Specification: Jan. 18, 1956.  
No. 1681/56.

Application made in United States of America on June 30, 1955.  
Complete Specification Published: Dec. 10, 1958.

Index at acceptance:—Class 2(5), R(3C13:3E:9C13).

International Classification:—C08g.

## COMPLETE SPECIFICATION

### Plasticised Linear Aromatic Polyester Compositions

We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organized under the Laws of the State of Ohio, United States of America, with offices at 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to plasticized linear aromatic polyesters.

Linear aromatic polyesters in the solid state at room temperature are normally hard, tough materials. Because of their hardness and general inflexibility these polyesters are considerably limited in their applications and find their chief utility in thin films or fibers wherein their inherent hardness and inflexibility are compensated for by the thinness of the particles or fibers. The addition of plasticizers to crystallizable polymers increases their rate of crystallization and it has been found that many of the materials that are commonly used as plasticizers for polymers such as the vinyl resins increase the rate of crystallization of the linear aromatic polyesters to such an extent that they cannot be incorporated into the crystalline polyesters. An extremely rapid rate of crystallization is undesirable because usually the polymer must be worked or stretched or cold-drawn while it is in the amorphous state in order to have the product acquire certain desired physical characteristics. In addition to affecting the rate of crystallization, many of the materials that are ordinarily used as plasticizers for other polymers are not compatible with the linear aromatic polyester resins and when incorporated in such a resin separate out leaving the resin in its original unplasticized state.

It is an object of this invention to provide improved linear aromatic polyester compositions. It is another object to provide novel plasticized linear aromatic polyester compositions. It is another object to provide polyester compositions having improved flow and pro-

[Price 3s. 6d.]

cessing properties. Other objects will appear hereinafter as the description of this invention proceeds.

The plasticizers of the invention can be incorporated in the polyester by various means. For example, the plasticizer can be added to a solution of the polymer in a suitable solvent, and the solvent can then be evaporated leaving the polymer homogeneously mixed with the plasticizer. In the case of polyesters having a low melting point and a low crystallization rate the plasticizer can be incorporated into the polyester by mixing the materials in a Banbury internal mixer or on a two-roll mill. In the case of copolymers having high melting points and rapid crystallization rates the plasticizer can be suitably incorporated in the polyester by heating the plasticizer and mixing it while hot with hot molten polyester as described in our co-pending application No. 1683/56 (Serial No. 805,588).

The practice of the invention is illustrated by the following examples, in which the proportions of the copolymer constituents are given as mol per cent.

#### EXAMPLE 1

Ten grams of a 60—40 ethylene terephthalate - ethylene isophthalate copolymer were blended with 2.0 grams of methyl phthalyl ethyl glycolate by mixing in a test tube at 171° C. The resulting mixture was then passed through a small mill a number of times to assure uniform blending, and was molded at 177° C. into a film. The molded film from this composition was clear and far more flexible than a control sample to which no plasticizer had been added.

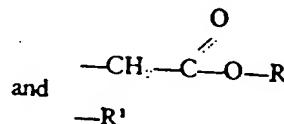
#### EXAMPLE 2

Ten grams of a 60—40 ethylene terephthalate - ethylene isophthalate copolyester were plasticized with 2.0 grams of ethyl phthalyl ethyl glycolate in the manner described in Example 1. The molded film from this composition was far more flexible than the control sample.

## EXAMPLE 3

Ten grams of a 60-40 ethylene terephthalate-ethylene isophthalate copolyester were mixed with 2 grams of butyl phthalyl butyl glycolate by the method described in Example 1. The molded film from this composition was more flexible than a control sample.

The phthalate esters suitable for use in this invention are those esters in which the alcohol residues have respectively the general formula



15 in which R and R' are the same or different radicals selected from the group consisting of alkyl radicals containing from one to four carbon atoms in the alkyl group, phenyl, tolyl, xylyl, benzyl and tetrahydrofurfuryl radicals.

20 Representative examples of esters of the class of this invention are methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate, propyl phthalyl propyl glycolate, butyl phthalyl butyl glycolate, phenyl phthalyl ethyl glycolate, tolyl phthalyl ethyl glycolate, xylyl phthalyl ethyl glycolate, benzyl phthalyl ethyl glycolate and tetrahydrofurfuryl phthalyl ethyl glycolate.

25 The polyesters with which this invention is concerned are the high molecular weight linear aromatic polyesters. The term "high molecular weight polyesters" is used in this specification and the appended claims to mean those polyesters having an intrinsic viscosity of at least 0.4 when measured at 30.0°C. in a solvent composed of a 60-40 w/w mixture of phenol and tetrachloroethane. Intrinsic viscosity is used as a measure of the degree of polymerization of the polyester and can be calculated using the Billmeyer extrapolation equation:

$$[\eta] - 1/4 \frac{\eta_{sp}}{C} + 3/4 \frac{\log \eta_r}{C}$$

in which  $[\eta]$ , intrinsic viscosity, is the limit

$$\frac{\eta_{sp}}{C} \quad \text{as} \quad \eta_{sp} \rightarrow 0$$

$$\eta_{sp} = (\eta_r - 1)$$

$$\frac{\text{Viscosity of solution}}{\text{Viscosity of solvent}}$$

and C is the concentration in grams of the polyester per 100 cc of the solution.

The term "aromatic polyester" whenever

employed in the specification and claims is intended to mean a polyester in which the recurring structural unit contains an aromatic nucleus. Examples of aromatic polyesters are the polyesters derived by the self-condensation of hydroxy acids such as para(beta-hydroxy ethoxy) benzoic acid, para-(hydroxy methyl) benzoic acid, and para-(beta-hydroxy ethyl) benzoic acid. Further examples are polyesters derived from the condensation of dicarboxylic acids such as terephthalic acid, isophthalic acid, 1,4-diphenoxy benzene-4',4"-dicarboxylic acid, 1,4-bis(phenoxy methyl)-benzene-4',4"-dicarboxylic acid, 1,4-bis(phenoxy methyl)-benzene-4,4'-dicarboxylic acid, phenoxy benzene-4,4'-dicarboxylic acid and diphenoxy alkane dicarboxylic acids with glycols such as ethylene glycol, trimethylene glycol, tetramethylene glycol and hexamethylene glycol. Further examples are polyesters derived from dihydroxy aromatic compounds such as hydroquinone and a dicarboxylic acid. Suitable derivatives of the acids such as the amides, acid chlorides, and the esters such as the methyl, ethyl, propyl, butyl, amyl and phenyl ester can be used. Various copolymers from these and similar reactants can also be used. The polyesters derived from terephthalic acid and isophthalic acid or ester-forming derivatives thereof with a glycol, and terephthalate-isophthalate copolymers constitute a preferred class. The invention has particular utility in its application to polymeric ethylene terephthalate and ethylene terephthalate-isophthalate copolymers, especially those copolymers in which the ethylene terephthalate units comprise from 90 to 40 mole percent of the sum of the ethylene terephthalate and ethylene isophthalate units and the ethylene isophthalate units comprise correspondingly from 10 to 60 mole percent of said sum.

While the plasticizers may be incorporated into the linear aromatic polyester over a wide range of concentrations, generally from 5 to 60% by weight of phthalate ester plasticizer, based on the polyester, is sufficient. The preferred range of plasticizer is from 10 to 40% by weight of the polyester.

The plasticized polyesters of this invention have many advantageous properties and can be used for coating or impregnating cloth, for molding applications such as housings for radios, clocks and cameras, and can also be used for molding phonograph records when the highly crystalline, rapidly crystallizable polyesters are used. Plasticized compositions from the polyesters having slower rates of crystallization can be used for wire coatings, and extruded or cast films which are useful in various packaging applications. The films can also be used for such applications as shower curtains, raincoats, aprons and table covers. Filaments of various of these compositions can be used in brushes, textiles, filters and in insect screening.

5 While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the scope of the invention, as defined in the appended claims.

which the phthalate ester is ethyl phthalyl ethyl glycolate.

4. A composition according to Claim 1 in which the phthalate ester is propyl phthalyl propyl glycolate.

5. A composition according to Claim 1 in which the phthalate ester is butyl phthalyl butyl glycolate.

6. A composition according to Claim 1 in which the phthalate ester plasticizer is present in amount of from 5 to 60% of the weight of the linear aromatic polyesters.

7. A composition according to any of Claims 1 to 6 in which the linear aromatic polyester is a polyester derived from terephthalic acid and/or isophthalic acid.

8. A composition according to Claim 7 in which the linear aromatic polyester is polymeric ethylene terephthalate.

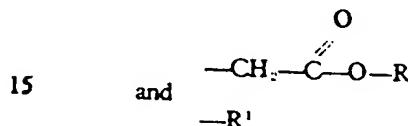
9. A composition according to Claim 7 in which the linear aromatic polyester is a co-polyester of ethylene terephthalate and ethylene isophthalate in which the ethylene terephthalate units comprises from 90 to 40 mole percent of the sum of the ethylene terephthalate and ethylene isophthalate units.

10. A linear aromatic polyester plasticised with a phthalate ester substantially in accordance with any of the foregoing examples.

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## WHAT WE CLAIM IS:-

10 1. A composition comprising a linear aromatic polyester plasticized with a phthalate ester in which the alcohol residues have respectively the general formula



in which R and R' are radicals selected from the group consisting of alkyl radicals containing from one to four carbon atoms, phenyl, tolyl, xylyl, benzyl and tetrahydrofurfuryl radicals.

2. A composition according to Claim 1 in which the phthalate ester is methyl phthalyl ethyl glycolate.

25 3. A composition according to Claim 1 in

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1958.  
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
copies may be obtained.